



## PATENT COOPERATION TREATY

PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P804032/WO/1	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/DE2003/003645	International filing date (day/month/year) 03 November 2003 (03.11.2003)	Priority date (day/month/year) 07 November 2002 (07.11.2002)
International Patent Classification (IPC) or national classification and IPC C23C 18/16		
Applicant MTU AERO ENGINES GMBH		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 9 sheets, including this cover sheet.

This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 1 sheets.

3. This report contains indications relating to the following items:

- I  Basis of the report
- II  Priority
- III  Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV  Lack of unity of invention
- V  Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI  Certain documents cited
- VII  Certain defects in the international application
- VIII  Certain observations on the international application

Date of submission of the demand 14 May 2004 (14.05.2004)	Date of completion of this report 17 January 2005 (17.01.2005)
Name and mailing address of the IPEA/EP	Authorized officer
Facsimile No.	Telephone No.

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/DE2003/003645

## I. Basis of the report

## 1. With regard to the elements of the international application:\*

- the international application as originally filed  
 the description:

pages \_\_\_\_\_ 1-11 \_\_\_\_\_, as originally filed  
 pages \_\_\_\_\_, filed with the demand  
 pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

- the claims:

pages \_\_\_\_\_ 2-8 \_\_\_\_\_, as originally filed  
 pages \_\_\_\_\_, as amended (together with any statement under Article 19)  
 pages \_\_\_\_\_, filed with the demand  
 pages \_\_\_\_\_ 1 \_\_\_\_\_, filed with the letter of 17 September 2004 (17.09.2004)

- the drawings:

pages \_\_\_\_\_, as originally filed  
 pages \_\_\_\_\_, filed with the demand  
 pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

- the sequence listing part of the description:

pages \_\_\_\_\_, as originally filed  
 pages \_\_\_\_\_, filed with the demand  
 pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

## 2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language \_\_\_\_\_ which is:

- the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).  
 the language of publication of the international application (under Rule 48.3(b)).  
 the language of the translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

## 3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.  
 filed together with the international application in computer readable form.  
 furnished subsequently to this Authority in written form.  
 furnished subsequently to this Authority in computer readable form.  
 The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.  
 The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4.  The amendments have resulted in the cancellation of:

- the description, pages \_\_\_\_\_  
 the claims, Nos. \_\_\_\_\_  
 the drawings, sheets/fig \_\_\_\_\_

5.  This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).\*\*

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rule 70.16 and 70.17).

\*\* Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.  
PCT/DE 03/03645

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

## 1. Statement

Novelty (N)	Claims	1-7	YES
	Claims	8	NO
Inventive step (IS)	Claims		YES
	Claims	1-7	NO
Industrial applicability (IA)	Claims	1-8	YES
	Claims		NO

## 2. Citations and explanations

1. This report makes reference to the following documents cited in the search report:

D1: DE-A-40 24 911 (ASEA BROWN BOVERI) 11 April 1991  
(1991-04-11)

D2: US-A-4 895 625 (THOMA MARTIN ET AL)  
23 January 1990 (1990-01-23)

D3: DE-A-37 16 935 (MOTOREN TURBINEN UNION)  
1 December 1988 (1988-12-01)

D4: SU-A-1 803 480 (DNEPROVSKIJ NII T MASH; N PROIZV  
OB EDINENIE MASH (SU)) 23 March 1993 (1993-03-23)

D5: EP-A-0 748 394 (SERMATECH INT INC)  
18 December 1996 (1996-12-18)

D6: WO-A-94/19583 (BAJ COATINGS LTD; FOSTER JOHN  
(GB); TAYLOR ALAN (GB); CHATTERLEY M)  
1 September 1994 (1994-09-01)

D7: US-A-5 935 407 (NENOV KRASSIMIR P ET AL)  
10 August 1999 (1999-08-10)

D8: WO-A-00/36180 (JOSSE PIERRE; BACOS MARIE PIERRE  
(FR); ONERA (OFF NAT AEROSPATIALE) 22 June 2000  
(2000-06-22).

## 2. Prior art.

2.1. D1 relates to the galvanic deposition of protective coatings on components of apparatus which are exposed to oxidation and corrosion at high temperatures, for example

components of turbines (column 1, lines 6 to 11). In embodiment 1, which is akin to the embodiment on page 10 of the present application, a gas turbine blade consisting of a nickel super alloy is first degreased and then anodically pickled in dilute HCl. An Ni bonding agent coating 1  $\mu\text{m}$  thick is then galvanically deposited. Then 150 g of an Ni/Al powder with a particle size of 10 to 50  $\mu\text{m}$  is suspended in 2.5 l of a nickel sulfamate bath. Deposition is carried out at a current density of 500 A/m<sup>2</sup>. To this end, the bath is vibrated. The glass beads added promote suspension as well as compacting the galvanically deposited coating. A coating 1 mm thick is produced and then diffusion annealed at 1100 °C for 3 h.

2.2. D2 discloses the production of protective coatings on components which are exposed to corrosive hot gas, for example gas turbine components (column, lines 7 to 9). To this end, according to claim 1 an electrolyte based on Co and/or Ni containing a passivated powder of a metal alloy of Al and/or Cr in suspension is prepared. The powder need not necessarily contain Cr. Passivation is taken to mean the provision of the particles with an artificial oxide layer. Following the galvanic deposition, the substrate is annealed. The powder has a particle size of 1 to 15  $\mu\text{m}$ .

2.3. D3 describes the production of a hot gas corrosion-resistant coating on, for example, turbine blades. To this end, TiSi<sub>2</sub> particles with a diameter of 0.5 to 50  $\mu\text{m}$  are suspended in an NiSO<sub>4</sub> or CoSO<sub>4</sub> electrolytic bath and a coating 10 to 1000  $\mu\text{m}$  thick is galvanically deposited. Annealing follows at 800 °C (column 2, lines 21 to 56).

2.4. D4 likewise indicates a process for improving the corrosion resistance of components which are exposed to hot gas. To this end, a mixture of Al and W particles is suspended in an Ni electrolyte and a protective coating is deposited and annealed at 1200 °C. The Al particles are treated with H<sub>2</sub>SO<sub>4</sub> prior to use, then washed and annealed in

air at 190 to 230 °C. An artificial oxide layer is thereby produced on the Al particles.

2.5. D5, which is cited in the present application, describes the improvement of the corrosion and oxidation properties of turbine components by application of a protective coating which consists of Al and Si particles and which is then diffused in by heat treatment [0001, 0002, 0039 to 0049]. A prior art protective coating which also consists of Al and Si particles is cited in [0012] and [0013].

2.6. Finally, it should be noted that it is prior art to improve the corrosion properties of components which are exposed to hot gas by means of protective coatings obtained by galvanic deposition of particles based on Cr-Al-Y and subsequent annealing (D6, D7). Currentless methods for depositing coatings of this kind are also known (D8).

### 3. Novelty (PCT Article 33(2)).

3.1. Claim 1 appears to be novel, because none of the documents D1 to D8 indicates external currentless or electrolytic deposition of Pt in which further particles are added.

3.2. Claim 8 does not appear to be novel, because there is no apparent difference between a protective coating produced by the method as per claim 1 and a coating produced by the method as per D5. In D5, a coating containing the metals which are also mentioned in claim 1 of the present application is successively deposited. That coating, like that of claim 1, is annealed to produce the final protective coating.

### 4. Inventive step (PCT Article 33(3)).

4.1. D1 to D4 indicate methods which contain all the technical features of claim 1, except that in D1 to D4 Ni

and/or Co instead of Pt are/is deposited by external currentless or electrolytic methods. D6 to D8 also indicate methods in which particles are deposited on a substrate together with a metal by external currentless or electrolytic deposition of said metal. In all cases D1 to D4 and D6 to D8, articles which are exposed to hot gas corrosion are coated.

Alloy formation is achieved and the protective coating is formed by subsequent annealing of the deposited coating.

4.2. It is sufficiently well known that the protective coatings of articles of this kind may also contain Pt. D5, for example, indicates that Pt is first **electrolytically** deposited on the surface of a suitable component, a slurry of Al and Si powder is then applied, and thereafter sintering is carried out at 660 °C [0046, 0040]. D8 also mentions the use of noble metals in coatings of this kind, Pt and Pd being preferred (claims 1 and 4).

4.3. It therefore seems obvious to also use Pt-containing electrolytes in conjunction with the methods mentioned D1 to D4 and D6 to D8 in the production of hot gas corrosion-resistant coatings in order to obtain a matrix of Pt-containing metal and particles which form said corrosion-resistant coating following an annealing step.

Moreover, D5 already suggests that consideration be given to the **electrolytic** deposition of Pt in order to form corrosion-resistant coatings of this kind.

And finally, the present application does not indicate any surprising effects which could be attributed to the use of Pt instead of Ni or Co in electrolytes.

4.4. The additional technical features of dependent claims 2 - 8 are already mentioned in documents D1 to D8 or can be discovered by routine experimentation.

D1, for instance, already indicates the use of Ni-alloyed particles with a particle size of 10 to 50 µm. In D2, a passivated powder, which therefore contains particles with an artificial oxide layer, is used. In D3, TiSi<sub>2</sub> particles are used as the powder. The use of Si particles to improve the corrosion properties is known from D5.

The determination of the optimal protective coating thickness is considered to be routine procedure.

4.5 Finally, it should be noted that it is prior art to improve the corrosion properties of components which are exposed to hot gas by means of protective coatings obtained by galvanic deposition of particles based on Cr-Al-Y and subsequent annealing (D6, D7). Currentless methods for depositing coatings of this kind are also known (D8). The exclusion of Cr as a constituent of the particles in claim 1 therefore seems to be merely an attempt to establish novelty over methods known per se. In any case, special non-obvious technical effects of the exclusion of Cr are not described in the present application. On the contrary: according to page 3, lines 15 and 16, Cr may even be present.

##### 5. Industrial applicability.

Claims 1 - 8 comply with the requirement of industrial applicability (PCT Article 33(4)), because the technical subject matter of the present application can be made in industry or, in a technical sense, used.

##### Box VII

##### **Certain defects in the international application**

The present application does not comply with the requirements of PCT Rule 5.1(a)(ii), because the introductory portion of the present application does not

cite the closest prior art, for example documents D1 to D3, or briefly outline the relevant prior art disclosed therein.

Box VIII

**Certain observations on the international application**

1. Clarity.

1.1. Claim 1 is inconsistent with the description, page 3, lines 15 and 16, according to which the particles preferably, but not necessarily, do not contain Cr.

1.2. The definition of the oxide coating thickness in claim 2 is vaguely worded: what are "normal environmental conditions"? This defect could be overcome if the thickness of the oxide layer were specified as on page 7, lines 23 to 25.

1.3. It makes little sense for claim 5 to be dependent on claim 4: Si particles which are alloyed with Si.

2. The present application does not comply with the requirements of PCT Article 5, because a person skilled in the art is not able to carry out the subject matter of claim 1. For instance, the application contains no embodiment showing how the deposition should be carried out with a Pt electrolyte and what electrolyte would be suitable for this purpose.